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The diagram of phase-field crystal structures: an influence of model parameters in a two-mode approximation

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Abstract. Effect of phase-field crystal model (PFC-model) parameters on the structure diagram is analyzed. The PFC-model is taken in a two-mode approximation and the construction of structure diagram follows from the free energy minimization and Maxwell thermodynamic rule. The diagram of structure's coexistence for three dimensional crystal structures [Body-Centered-Cubic (BCC), Face-Centered-Cubic (FCC) and homogeneous structures] are constructed. An influence of the model parameters, including the stability parameters, are discussed. A question about the structure diagram construction using the two-mode PFC-model with the application to real materials is established.

1. Introduction

The phase-field crystal model (PFC-model) is suitable for simulations of the dynamics of atomic densities on the diffusion time scales. This model can be used to calculate the coexistence of structures having various crystal lattices and to model a wide spectrum of processes [1].

The amplitude's approximation for the PFC-model is based on the limitation of the periodic atomic density field by the amplitude envelope as a non-conserved order parameter. The PFC-model [2–5] was formulated to describe continual transitions from the homogeneous to the periodic crystal state (similarly to the Landau–Brazovskii transition [6–8]) and between different periodic states [9] over diffusion times. The model can be derived as a reformulation of the Swift-Hohenberg equation for the thermal fluctuation fields [10] or it follows as a first approximation of the Density Functional Theory [11–13]. The model uses the free energy as functional of the atomic density field which is n-periodic in the solid (crystal) phase and homogeneous in the liquid state. Periodicity of the field n naturally takes into account the elastic energy and symmetry of crystals that is described as the motion equation for the conservative order parameter. In such a way, it is possible to simulate a wide class of phenomena including, e.g., epitaxial growth and ordering of nanostructures on micrometer scales [9], crystallization and high-speed regimes of front propagation [14, 15], the motion of dislocations and plastic flow, the formation of a disordered amorphous state, premelting of grain boundaries, crack spreading, rearrangement of microscopic structure of interfaces, and the dynamics of colloidal systems and polymers [16].

The determination of equilibrium structures and their coexistence in "average atomic density–transition driving force" diagrams takes a special place in the phase-field model. Such diagrams determine the structures to which unstable or metastable states of a material must evolve. Diagrams of two dimensional crystalline structures for transitions from an unstable state were constructed using the atomic density functional, amplitude expansion and the Maxwell equal-area rule [3, 17]. The structural diagram for transitions for two-mode functionals from the metastable state was also constructed earlier for different control parameters [1, 18–22]. In the present study, for the structure diagram construction, we use a numerical method for minimizing of free energy functionals. This method makes it possible to determine the parameter range for the existence of three dimensional structures in materials. Using the free energy functional in two-mode approximation (that extends our previous study [23]), the construction for the coexistence of homogeneous (liquid) phase, Body-Centered-Cubic (BCC), Face-Centered-Cubic (FCC) crystal lattices of materials is made. The structure diagram is constructed in coordinates "temperature – atomic density".

2. Free energy for crystalline states

To evaluate the various properties of the different crystal states it is useful to use two-mode approximation (accounting a second atomic coordination sphere) instead of the original one-mode PFC approximation. Using this approximation we can construct the set of the free energy functionals for the given phases in the equilibrium state. This approach lead to the more accurate and exact calculations for complex crystal structures.

The free energy functional for the first-order phase transformations is given by [1, 18, 20]

$$F(n,T)=\int_V dV\left(\Delta B_0\frac{n^2}{2}+B_0^x\frac{n}{2}\mathfrak{D}_i n-2a\frac{n^3}{3}+15v\frac{n^4}{4}\right), \tag{1}$$

where the $n=(\rho-\rho_{liquid})/\rho_{liquid}$ is dimensionless atomic density, ρ is the local atomic density, ρ_{liquid} is the reference atomic density of the homogeneous state (liquid), $\Delta B_0=B_0^\ell-B_0^x$ is the driving force taken as a difference of compressibility and elastic modulus of system, a and v are phenomenological parameters which can be selected for certain type of material. To describe the energy of crystal we introduce the nonlinear operator $\mathfrak{D}_i$:

$$\mathfrak{D}_i=\begin{cases} r_0+(q_0^2+\nabla^2)^2, & \text{one-mode approximation, i=1,}\\ [r_0+(q_0^2+\nabla^2)^2][r_1+(q_1^2+\nabla^2)^2], & \text{two-mode approximation, i=2,}\end{cases} \tag{2}$$

where r_0 and r_1 are shifts of the first two wave vectors, responsible for the relative stability of structures, and q_0 and q_1 are the modules of first two sublattice wave vectors. This extension of the previously introduced two-mode PFC model (Wu et al. [20] with $r_0=0$) has been proposed by Asadi and Zaeem [21]. The role of the parameter r_0 will be revealed below, here we just can mention that r_0 can be used for the exact minimization of the free energy by the parameter q to find the wave number of the equilibrium state for the crystal or homogeneous (liquid) phase.

To get a compact and dimensionless form of the free energy (1), it is convenient to use the following substitutions:

$$\tilde{n}=\sqrt{\frac{15v}{B_0^x}}\left(n-\frac{2a}{45v}\right),\quad \varepsilon=\frac{1}{B_0^x}\left(\frac{4a^2}{45v}-\Delta B_0\right),\quad F(n,\Delta B_0)\to\mathfrak{F}(\tilde{n},\varepsilon). \tag{3}$$

Hence the free energy (1) transforms to

$$\mathfrak{F}=\int dV\left(\frac{\tilde{n}}{2}[-\varepsilon+\mathfrak{D}_i]\tilde{n}+\frac{\tilde{n}^4}{4}\right), \tag{4}$$

where we neglect the high order terms for the simplicity. Then the dimensionless operators $\mathfrak{D}_i$ (2) are:

$$\mathfrak{D}_i \begin{cases} (1+\nabla^2)^2, & \text{one-mode approximation, i=1,} \\ [R_0+(1+\nabla^2)^2][R_1+(Q_1^2+\nabla^2)^2], & \text{two-mode approximation, i=2,} \end{cases} \tag{5}$$

with $R_0 = r_0/q_0^4$, $R_1 = r_1/q_0^4$, $Q_1 = q_1/q_0$.

As a result, the free energy (4) with $\mathfrak{D}_2$ from eq. (5) has three parameters: R_0, R_1 and ε. The first two parameters control the stability of structures. The third parameter, as the driving force parameter ε, is the relative temperature $\varepsilon = (T_c - T)/T$ which determines the excess over the transition temperature $T = T_c$ and the relation between elastic properties of the system in terms of quantities ΔB_0 and B_0^x. In the next section we will use the two-mode form of the functional which implies the form of the amplitude's expansion coefficients and number of the parameters.

3. Crystalline structure determination and selection of parameters

Using the summation of reciprocal lattice vectors [1,19,21] we can make the amplitude expansion and get the dimensionless density profiles indicating the symmetry and properties of a given phase (homogeneous, BCC, FCC):

$$n_{homogeneous} = \tilde{n}, \tag{6}$$

$$\begin{aligned} n_{BCC} = \tilde{n} + 4\eta_1 &\left[\cos(qx)\cos(qy) + \cos(qx)\cos(qz) + \cos(qy)\cos(qz)\right] \\ &+2\eta_2\left[\cos(2qx) + \cos(2qy) + \cos(2qz)\right], \end{aligned} \tag{7}$$

$$n_{FCC} = \tilde{n} + 4\eta_1\cos(qx)\cos(qy)\cos(qz) + \eta_2\left[\cos(2qx) + \cos(2qy) + \cos(2qz)\right], \tag{8}$$

where η_1 and η_2 are the density amplitudes for the first and second reciprocal lattice vectors and q is the unit cell size. Substituting Eqs. (6-8) into the free energy (4) with $\mathfrak{D}_2$ from Eq. (5) and integrating over the elementary cell with size $2\pi/q_{eq}$ one gets the free energy for every phase which depends of the equilibrium lattice number q_{eq}.

In one-mode approximation, the wave number q_{eq} can be found by minimization of free energy analytically. In the two-mode approximation, obtaining of q_{eq} can be made only numerically. The work [21] proposes the way to minimize the functional by accepting the parameters $q_{eq,BCC} = 1/\sqrt{2}$ and $q_{eq,FCC} = 1/\sqrt{3}$ [18–20] and to correct the minimization error $\partial\mathfrak{F}/\partial q_{eq}|_{q_{eq}} \neq 0$. Asadi and Zaeem [19, 21] suggest to introduce the condition for R_0 as:

$$\left.\frac{\partial\mathfrak{F}}{\partial q_{eq}}\right|_{q_{eq}} = 0 \quad \Rightarrow \quad R_0 = R_1\frac{\eta_2^2}{\eta_1^2}. \tag{9}$$

In this way it is possible to prevent the minimization error and incorporate the condition on the R_0 parameter value at the same time. The model of Mkhonta et al. [24] for the multi-mode PFC approximation states parameters b_1 and b_2 as independent. These parameters are similar to the R_0 and R_1 in our model for number of modes $N = 2$. Therefore, we are calculating structure diagrams using the approaches of Asadi-Zaeem and Mkhonta et al., i.e., we shall use the dependent R_0 by (9) and the independent case for positive and negative values of R_0.

Because interplanar distances are different for different crystal structures we utilize the relevant $Q_{1,BCC} = \sqrt{2}$, $Q_{1,FCC} = 2/\sqrt{3}$ for each phase. For the homogeneous phase, the parameter Q_1 is given by the coexistent crystalline phase. The minimization procedure of $\mathfrak{F}$ with regard to the density amplitudes η_1 and η_2 is given by the gradient descent algorithm. This

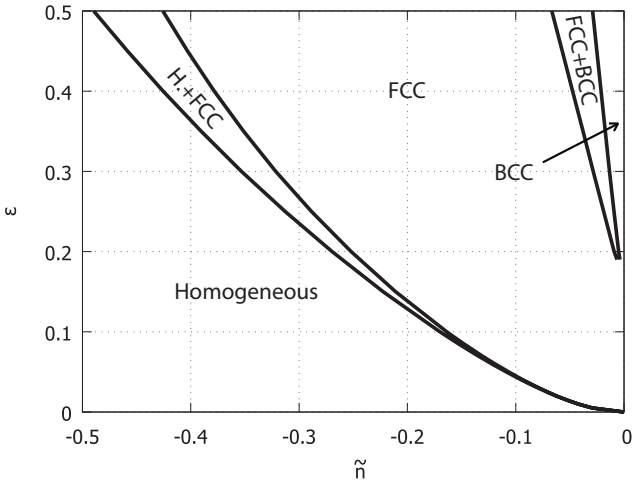

Figure 1. The structure phase diagram for BCC, homogeneous (liquid), FCC-structures at $R_1 = 0.05$ with the approximation for the R_0 to dispose the wave number minimization error. The parameter Q_1 is taken as different for corresponding phases. In high-temperature region (small $\varepsilon = 0..0.15$), the stable BCC-structure is absent (due to $\mathfrak{F}_{FCC} < \mathfrak{F}_{BCC}$). For this set of parameters and approximations, the high temperature transformation of BCC-FCC is absent. The phase transition at much lower temperature T, namely at $\varepsilon = 0.2$, between BCC- and FCC-structures appears in the solid state similarly to the low temperature FCC-BCC phase transitions in a pure iron. Label "H." on the diagram means "homogeneous".

predict the stable structure's coexistence for obtained amplitudes even for small values of ε and negative values of R_0 and R_1. Using the obtained amplitudes we find the free energy functionals for each phase $\mathfrak{F}_{homogeneous}(\varepsilon, \tilde{n}, R_0, R_1)$, $\mathfrak{F}_{BCC}(\varepsilon, \tilde{n}, R_0, R_1)$, $\mathfrak{F}_{FCC}(\varepsilon, \tilde{n}, R_0, R_1)$. With these free energies, we construct the diagram of crystal structures with their coexistence at values of $R_0 = -0.1, 0, 0.1$ and $R_1 = -0.1, 0, 0.1$ for independent R_0 case; and $R_1 = 0, 0.05, 0.1$ for the dependent parameter R_0.

4. Construction of structure diagram and discussion

4.1. Structure diagram for three dimensional crystals

In this section the structure diagrams are calculated using the solution of the Maxwell area rule, using the chemical potentials and free energy functionals for each phase. The selection mechanism is based on the thermodynamic rule of the minimal energy for a virtually existed structure.

Figure 1 shows the domains of existence of the homogeneous (liquid) phase, the crystalline BCC structure and FCC structure in coordinates "normalized average atomic density $\tilde{n}$ vs. dimensionless temperature ε" for the dependent parameter R_0 and $R_1 = 0.05$. We calculate the coexistence separately for the each pair of the structure and then select the structure by its minimal free energy. For the positive R_1, the BCC region is located in the region of large ε. This region decreases with the decrease of R_1 to the zero. The condition on the parameter R_0 prevents shifting of the BCC structure region under the FCC area. With large negative values of R_0, the BCC-structure becomes unstable.

4.2. Structure phase diagram for the independent control parameter R_0

Figure 2 presents the structure diagram for the phases with independent values of $R_0 = -0.1$ and $R_1 = -0.1$. We calculated a set of diagrams to find the influence of parameters R_0 and R_1 on the position of lines for coexisted structures. Note that the parameter Q_1 has to be chosen exactly for a given structure to take in account the symmetry of the density profile and the correct free energy of a structure. For the presently constructed diagrams, the overlapping of

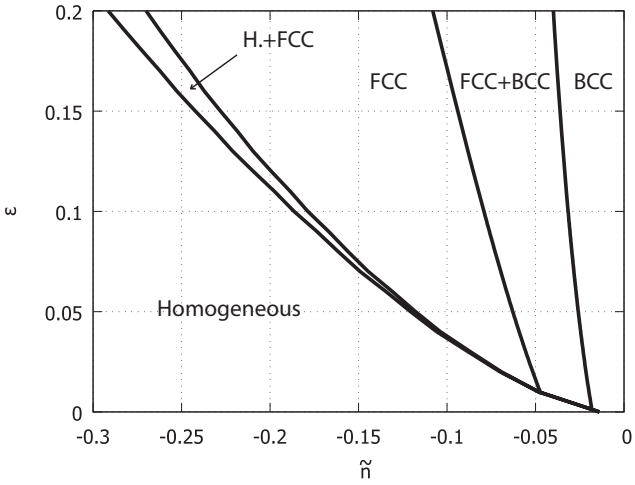

Figure 2. The structure diagram for BCC, homogeneous (liquid), FCC-structures at $R_0 = -0.1, R_1 = -0.1$. The parameter Q_1 is taken different for corresponding phases. The region of existence of the BCC structure is enlarged relatively to the Fig. 1 and it shows the possibilities of the coexistence of BCC and homogeneous structure. Nevertheless there is no alternation in structures with the increase of ε at the fixed $\tilde{n}$. For the complicated sequence of phase transformations in the region of small undercoolings $\varepsilon = 0 \div 0.15$, one can expect that FCC-BCC-FCC can appear when the parameter R_0 is free. Label "H." on the diagram means "homogeneous".

regions BCC-FCC-BCC is absent. At small undercooling, i.e. at high temperature the sequence of structures should be BCC-FCC (i.e., high temperature ferrite – austenite in the pure iron). The possible opportunity to obtain such sequence is to introduce in the model an additional atomic interaction (which may lead to appearing of additional structural transformation).

For the positive values of R_0 and R_1, the BCC region is located in the region of large ε, the lines of coexisted structures do not changed dramatically compared to the Fig. 1. The same situation is observed for the positive R_1 and fixed R_0. The independent parameter R_0 successfully controls the width of BCC zone and location of the lower part of the region. Simultaneous converging of the parameters to zero leads to widening and getting down of the permitted BCC region. With the positive values of the R_1 there is no strong influence of the $R_0 = 0$ on the form of the coexisted curves. The negative values of the parameter R_1 allows us to broad the BCC region and to enhance the incline of the "FCC+Homogeneous" line. For independent values of R_0, there is no limitation for the width of the BCC zone. This leads to appearance of the "Homogeneous(Liquid)-BCC" transition (small $\varepsilon < 0.02$ in Fig. 2). The "FCC+Homogeneous(Liquid)" structure detaches the BCC region following the thermodynamic phase selection rule.

5. Conclusions

Structure diagrams were calculated for the two-mode PFC model with different control parameters. These parameters are linked with stability of the three dimensional crystal structures.

The parameter R_0 can be dependent that limits the ability to form complex crystal coexistence with small values of the driving force ε. On the other hand, we can reduce the degrees of freedom of the entire system. In such procedure, the reduction of the minimization error is very important.

We have shown the possibilities to find the equilibrium structure diagrams for independent parameter R_0. With this aim we have used the numerical minimization of the density amplitudes in the dimensionless atomic density expansion. The resulting diagram showed the stable solution for the coexisted curves in the wide region of driving force.

The pair of parameters R_0 and R_1 gives the capability to vary the properties of the material. Despite of the minimization error, it seems to be necessary to separate R_0 and R_1 making

R_0 as independent parameter. Minimization error could be corrected during the numerical minimization of amplitudes. The proposed method makes it possible to extend the diagrams description of the complex three dimensional crystalline structures using the two-mode PFC-model.

6. References

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